

Dielectric Loss Microwave Degradation of Polymers: Cellulose

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Synopsis

The pyrolysis of organic waste polymers to produce fuels and chemicals is of interest to augment petroleum-based processes. The wide variety of pyrolysis products of low yield and the uncertain role that heat transfer rate plays in determining these have been deterrents to utilization in the past. A possible approach to increased selectivity for products is to heat them rapidly and homogeneously with the aim of narrowing the product distribution. A very rapid means of homogeneous heat transfer throughout the substrate is microwave heating. A laboratory study has been done to determine what effect high-intensity microwave energy has on the thermal degradative pathways of cellulose. The product distribution found when cellulose is pyrolyzed in the absence of a microwave discharge is similar to that found in conventional furnace pyrolysis. The major products are levoglucosan (27%), carbon dioxide (2–5%), water, and charred residue. However, the total heat-up and reaction times for even large pellets are reduced to less than 2–3 min when high-intensity microwave irradiation is employed. Effects of pressure and microwave power are reported. Low external gas temperature also prevents secondary reactions.

INTRODUCTION

Thermal Degradation of Cellulose

The roles that heating rate and temperature play in determining favorable processing conditions for the thermochemical conversion of cellulosic materials to useful fuels and chemicals are largely ill-defined and difficult to study. Ambiguity arises when one examines the wide variation in pyrolysis kinetic parameters for biomass and its fractions, such as cellulose. The occurrence of low activation energies and the profusion of suggested mechanisms and varying product distributions for the same apparent pyrolysis conditions may indicate that limitations imposed by heat and mass transport rates in some studies are not given full consideration. Dry wood is an extremely poor heat transfer medium, especially in the large particle sizes that would not add costly size reduction steps to a thermal degradation process. When realistic particle sizes are studied, slow heat conduction retards the reaction rate and the escape of volatile products from the pellet may be too slow to allow desired early reaction products to be transported from the reaction zone before undesired secondary reactions occur. Thus, it is difficult to distinguish primary volatiles from secondary reaction products. Few experimental studies have systematically investigated the process variables such as particle size, heat transfer rates, and ultimate temperatures with a view to studying their interactions and effects on the competitive reaction

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rates which may alter the product distribution obtained in cellulose pyrolysis. Wen and Tone¹ have summarized experimental results that show that char, tar, and gas yields are affected by both heating rate and temperature in coal pyrolysis. Panton and Rittman² mathematically modeled the pyrolysis of a "thermally" thick slab of porous material to simulate cellulose pyrolysis. Product distributions from the model using three reaction scheme were sensitive to the temperature profile in the porous slab and the applied heat flux. The same would presumably be true for cellulose and other biomass fractions.

Most conventional biomass pyrolysis studies heat the wood chips or solid particles by convective heat transfer from the gas and by conduction from the substrate surface to the unreacted core. At high temperature in large particles, this process is often slower than reaction rate³⁻⁶ because of the very low thermal diffusivity of dry wood. Some studies report heating times as long as days,⁷ possibly chosen to avoid temperature gradients. During such long heat-up periods one must apply the techniques of nonisothermal kinetics used by Connors et al.⁸ in their hydrocracking studies of lignin.

Owing to the large number of low yield products, it is difficult to measure quantitatively and relate to heating rate and temperature all degradation products of complex polymers such as cellulose. Often a larger sample is used to increase the accuracy of the analysis scheme, but this can introduce nonisothermal behavior due to slow heat transfer rates. The study of small or thin samples are most often reported in the literature.⁷ However, the reaction products from large samples subjected to identical experiments may not be the same because of the different secondary reactions experienced by the hot primary volatiles confined to the interior of a large sample. Thus, there is a need to identify the effects that particle size and heat transfer rate have on the reaction sequences and ultimate product distribution.

The literature on cellulose pyrolysis products has been reviewed elsewhere.^{4,5,7-16} Studies by Shafizadeh et al.,^{10,11} by Broido,¹² have focused on the details of the bond scission in the carbohydrate molecules and the kinetic coefficients of those steps. Two studies^{10,11} have reported high levoglucosan yields from low-temperature cellulose degradation and proposed a kinetic model for its formation. The nonisothermal heating times in this study were rather large, however. Franklin¹³ has directly identified cellulose primary pyrolysis products using a mass spectrometer. Antal and co-workers¹⁴ have measured the formation rates of other products, primarily gas phase products, in the steam gasification of cellulose. Lewellyn et al.⁷ added to the understanding of cellulose degradation by studying the effect of heating rate on the pyrolysis of very thin samples. For their system, free of mass transfer limitations, the heating rate was found to have little effect on the reaction rate and little char resulted. Other product yields were not reported. Tang, using thermogravimetric analysis, found, however, that lower heating rates increased char yields.^{15,16} This is consistent with the char yield (37%) obtained by Bradbury et al.¹⁰ using apparently slower heating rates.

An interesting and unusual alternative is to cause rapid heat transfer by spatially uniform or volume heating a large biomass pellet with microwave energy deposition in the dielectric loss mode of heating.¹⁷ This rapidly imposes an unusual heat transfer situation in which the particle interior is hotter than the surroundings and primary volatiles are rapidly quenched upon escaping the solid.

It is the intent of this article to examine in a qualitative way the effect on pyrolysis product distribution when an unusual heat transfer and a typical mass transfer situation are imposed on a large biomass pellet. Tang reports that exothermic reactions of biomass occur. This exotherm also causes internal heating of the biomass pellet. However, this internal heating is usually small in comparison to the external heating of the particle by hot gases or a conventional furnace.^{4,5} Thus, the primary volatiles are exposed to high temperature surroundings upon escaping from the pellet and secondary reactions can then occur.

In this work, the emphasis is not on the technique of microwave heating but rather on what effect an unusual heat transfer situation has on the reaction rate and product distribution in the realistic situation of large-particle biomass pyrolysis. The design and optimization of microwave cavities and applicators is beyond the scope of this work. The results of this study are more general in that the focus is on the role that volume heating of a rather poor heat transfer medium—wood—has on pyrolysis. In this way the heat transfer can be improved without changing the mass transfer or rate of escape of volatiles. Thus, one can begin to see the uncoupled effects of these phenomena on reaction pathways. The results reported here will emphasize detailed product analysis and the extent to which volume heating influences rates. Models of the heat transfer aspects are reported elsewhere.³⁵

Dielectric Loss Microwave Heating of Materials

Microwave heating has been used for commercial drying for some time.¹⁷ Microwave-induced chemical transformations have been studied previously, but many of these studies have been limited to low pressure where a microwave plasma forms. These studies are reviewed in Graef¹⁸ and Graef et al.¹⁹ The dielectric loss microwave-induced reactions will be briefly discussed here.

Microwave energy has been used to obtain temperatures greater than 1700°C in alumina refractory materials.²⁰ In this study, it was estimated that the conversion efficiency of microwave energy to thermal energy was 90%, and 95% less energy was used when compared to conventional thermal means. Pei and Ford²¹ found that solid materials like coal and molybdenum disulfide could easily be heated to temperatures greater than 1900°C with a 2.5-kW microwave generator (2450 MHz). Che²² examined the microwave pyrolysis of coal and concluded that the severity of pyrolysis by microwave energy was greater than that obtained using a conventional furnace.

These studies on coal and inorganic materials indicate that pyrolytic temperatures can easily be achieved using microwave energy, but until recently, the use of this type of energy on polymeric or agricultural materials has largely been confined to nondestructive low power heating, moisture detection, freeze drying and induced polymerization.²³⁻²⁶ Tsutsumi²⁷ successfully converted polyethylene into a mixture of ethylene, propylene, and various other low-molecular-weight gases using a microwave reactor and sodium hydroxide as an additive. He also found microwave irradiation to be very effective for desulfurization of heavy oils and the depolymerization of scrap rubber. The Goodyear Corporation has a patented process to devulcanize and reclaim scrap rubber.²⁸ The authors are aware of no published data concerning microwave pyrolysis of cellulose. However, preliminary experiments have been conducted on cellulose in a water sus-

pension. The mixture was exposed to high-intensity microwave power and a black oily substance was recovered, but an analysis of the pyrolytic "oil" was not revealed.²⁹

The mechanism through which microwave energy is transformed into thermal energy is based upon the induced or permanent dipole moment of molecules. For macromolecules like cellulose, the polarity can be considered internal because only small segments of the entire molecule are responsive to microwave fields. When polar molecules are subjected to a strong alternating electric field, the displaced positive and negative charges will tend to orient themselves in a direction opposite that of the applied field. The point of maximum polarization occurs when all dipoles, whether induced or permanent, react to the applied field and are aligned. In practice, complete alignment is difficult to achieve because of the simultaneous effects of restricted mobility, thermal agitation, Brownian movement, and collision. The degree of alignment is also affected by the size of the molecule, the frequency of the radiation, and the viscosity or solidity of the surrounding medium. For high polymers, only the noncrystalline molecular segments align with the external field. In crystalline regions, the molecules are usually fixed with such rigidity that little or no orientation of the dipoles is possible.^{17,30}

The microwave energy that is dissipated in the form of heat is a result of elastic distortions, deformations, and displacements which occur as the molecules attempt to realign themselves after the stimulation by the strong alternating electric fields. The relaxation time after alignment depends on the viscosity of the medium, which in turn depends on the temperature. Because of this, the amount of microwave energy absorbed will be temperature dependent.^{17,30}

The dielectric properties of a material can be described by a complex ($j^2 = -1$) dielectric constant $\epsilon = \epsilon' - j\epsilon''$. The real part ϵ' directly influences the amount of energy that can be stored in a material in the form of an electric field, whereas the imaginary part ϵ'' , also called the loss factor, is a direct measure of how much energy a material can dissipate in the form of heat.

For an imposed electric field varying at an angular frequency of ω rad/sec, the dielectric constant decreases as the frequency f ($\omega = 2\pi f$) increases. The energy absorption passes through a maximum that is related to the relaxation time. The maximum absorption for many materials occurs at the frequency where $\omega = 1/t$, and t is the relaxation time.¹⁷ The polarization of small molecules in low viscosity media would show maximum energy absorption near microwave frequencies, while larger molecules in viscous media would show maxima at frequencies lower than those of microwave. The relaxation times of polymers, like cellulose, commonly have a wide distribution of values, and the corresponding dielectric loss is therefore smaller but occurs over a much wider frequency range.³⁰ At low frequencies (60 Hz), there is time for the system to become polarized with the field and high dielectric constants are observed. At intermediate frequencies, approximately in the microwave region of the electromagnetic spectrum, partial orientation occurs, giving the intermediate dielectric constant values of microwave heating. At very high frequencies above the microwave region, the response times are much too slow and polarization tends to disappear. Although it would be advantageous to choose the frequency of microwave irradiation in such a way as to break selected bonds, interference with communications has dictated that only 2450- and 915-MHz high-power generators be manufactured. Some im-

provement in absorption is to be gained using a resonance cavity for irradiation, but the need to scale up reactors precludes certain geometries. The type of energy deposition of an *S*-band waveguide (used here) shows promise for future scale-up.

When materials are placed in the path of microwaves, the material will absorb energy from the waves in proportion to its loss factor. If adequate power is available at the correct frequency, there will be a dramatic rate of heating throughout the sample volume. The power absorption per unit volume (W/m^3) can be expressed as

$$P = 55.63 f E^2 \epsilon'' \quad (1)$$

where f is the frequency (MHz), E is the rms electrical field intensity (kV/m), and ϵ'' is the dielectric loss factor. One of the characteristics which makes microwave heating rapid is that materials are heated more or less uniformly throughout the entire volume. For low thermal conductivity materials, this produces a smaller heat-up time. However, whether or not the heating of a given volume of substance will actually be independent of thermal conduction depends upon the depth of penetration of the microwaves, which for cellulose is 2.4 m at 2450 MHz.¹⁷ Thus, under conditions where microwave energy couples rapidly, the potential for quickly processing large particles of solid feedstocks exists.

It is also important to assess how microwave pyrolysis may possibly affect reaction product distribution. Because the dielectric loss factor depends on chemical structure for complex substances such as cellulose and its reaction products, selective heating occurs. Owing to the time-dependent chemical composition, the response of the material in the microwave field will also change and a rather different temperature-time history may be experienced by some components. This may in turn influence the degree of degradation of certain product fractions. The volume heating and volatiles outflow driven by high internal gas pressures may cause such a rapid escape of volatiles that the secondary reaction and cracking on the hot char surfaces surrounding typical pellets may not occur. The rather slow heat-up processes described in Lipska,³¹ and Arthur,³² and Broido¹² can be speeded, and the impact of greatly lessened internal temperature gradients can be assessed.

EXPERIMENTAL

Microwave Application System and Reactor

A Gerling-Moore model 4003 variable 0–2.5-kW power generator operating at 2450 ± 50 MHz was used to provide microwave heating. The 2.54-cm-i.d. quartz reactor passed diagonally through the broad faces of a 61-cm section of rectangular (7×3.2 cm) *S*-band waveguide. An impedance matching load, continuously recorded power monitors, and a triple-stub tuner were mounted in the waveguide, as shown in Figure 1. A cellulose or biomass pellet was placed

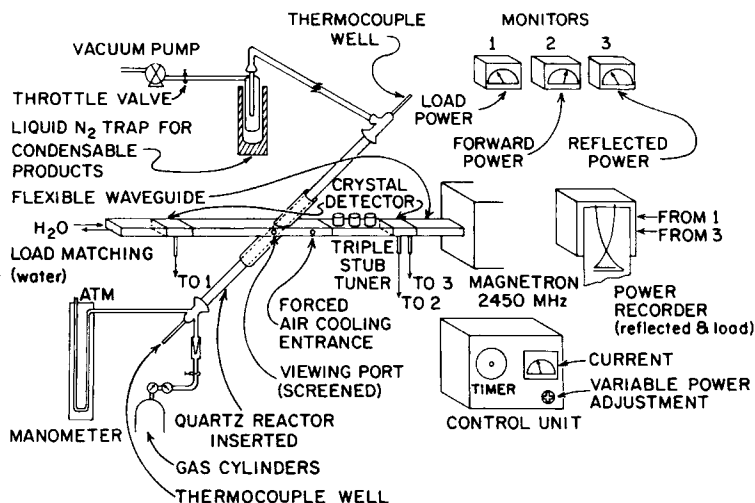


Fig. 1. Microwave circuit and gas handling system.

in the microwave field by sliding the material over a 3-mm o.d. Pyrex thermocouple well that was located in the center of the quartz reaction tube.

Because metallic objects could not be placed in the reaction zone without disturbing the field patterns, conventional thermocouple temperature measurements were somewhat of a problem. Local arcing and heating caused thermocouples and thermistors to give inaccurate results when placed in a region of microwave activity,^{33,34} especially at the higher field strengths used here. In order to get an indication of the temperatures achieved within the system, two chromel–alumel thermocouples (28 gauge) were used. One thermocouple was placed directly in the passing gas, a short distance downstream from the reaction zone. When placed upstream too far, the leads of the thermocouple served as an antenna, and an energy level much greater than the recommended safe level of 10 W/cm² was detected by a leakage monitor (Holaday Industries, Inc. model HI-1500). Because of this limitation, the thermocouple had to be placed 9 cm away from the center of the material being pyrolyzed. Although this method gave only an indication of the temperature of the devolatilized material, it was valuable in that a qualitative time–temperature response was found.

In one experiment, a chromel–alumel thermocouple was slid down the center of the 3-mm support rod and placed in the middle of the cellulose pellet while the microwave energy was temporarily shut off. The intermittent nature of the measurement and the inherent error resulting from cooling when the field was off gave less than satisfactory results. However, while the temperatures are not exact, the time–temperature curve shape is of interest. Wiggins³⁵ improved temperature measurements by employing an infrared pyrometer as described in other studies.³³

Dried helium was used as a carried gas to sweep out and quench reaction products. The pressure within the reaction zone was controlled by adjusting inlet valves to a vacuum pump, and the mass flow rate was set at 0.249 g/hr for all experiments. Pressures were monitored with a manometer.³⁶

Procedure

Ash-free analytical filter pulp (Carl Schleicher and Schuell Co., ash content less than 0.01%) was used as a source of cellulose. This material was dried under vacuum conditions at a temperature of 55°C in the presence of phosphorus pentoxide for several days prior to use. To reduce surface heat losses during pyrolysis, the cellulose pulp was compressed into solid cylindrical pellets 1.27 cm in diameter, weighing 2.6 ± 0.05 g.

After the desired pyrolysis exposure time, the microwave energy was terminated, and no further changes were made for a period of 10 min. The gas purge was then discontinued, and the system was evacuated for a period of 1 hr. The volatile compounds that collected on the cool walls of the reaction vessel were removed and trapped in a liquid nitrogen condenser placed immediately after the reaction zone.

After this 1-hr evacuation period, the pressure inside the system was increased to 250 torr and the material within the cold trap was isolated by closing inlet and outlet valves. The trap was removed from the liquid nitrogen and placed in an ice bath, and after temperature equilibrium was achieved, the gas inside the condenser was sampled and analyzed by gas chromatographic techniques. The gaseous compounds were then displaced from the condenser, and the yield of the material remaining at 0°C was determined by weighing the cold trap before and after each run.

The products not removed from the reaction vessel by the application of reduced pressures were extracted with acetone followed by methanol. The material recovered after removing the solvent was collectively designated "tar." All material remaining in the reaction zone after this extraction procedure was characterized as "charred residue."

Product Analysis

To analyze the pyrolysis products, infrared, ultraviolet, chromatographic, and mass spectrometric techniques were employed. The aqueous liquid products were analyzed using a Carbowax 20-*M* support coated open tubular column (SCOT column). The gaseous products were analyzed using a stainless steel column (6 ft \times 0.125 in.) packed with Porapak Q (150–200 mesh). Trimethylsilyl derivatives of the tars were prepared following the procedure outlined by Sweeley,³⁷ and the resolution of these compounds was obtained using an OV-1 SCOT column. Identification of the various pyrolysis products was made by comparing retention times and similarities in the ion fragmentation patterns using a Perkin-Elmer 990 coupled to a Hitachi Perkin-Elmer KMS-4 mass spectrometer.

RESULTS AND DISCUSSION

Absorbed Power and Temperature Effects on Reaction

Our early experiments showed that the surface-to-mass relationship was very important in microwave heating. Like most other high-temperature chemical processes, surface heat losses must be kept to a minimum to economically achieve the desired temperature response. Owing to the rapid outflow of volatiles

through the porous pellet from volume heating, considerable convective cooling occurred. Identical experiments were done using extraction thimbles and cellulose filter pulp (Whatman) compressed into solid cylindrical pellets. The same weight of material was loaded into the reactor for all experiments, but the surface-to-mass ratio of the extraction thimbles was $10.5 \text{ cm}^2/\text{g}$, while that of the cellulose pellets was approximately $2.8 \text{ cm}^2/\text{g}$. At a power density of $130 \text{ W}/\text{cm}^2$ per cm^2 of waveguide cross section and exposure time of 5 min, only 30% of the low density material was volatilized, while 72% of the cellulose pellet was volatilized.

This behavior can be explained by the fact that pure cellulose, when thoroughly dried, has a very low dielectric loss factor, limiting the amount of energy that can be dissipated in the form of heat. For large surface areas, heat losses owing to convection can easily reach levels equal to the amount of energy transformed. However, if a large amount of cellulose is confined in a small volume, high internal temperatures can be achieved within a very short time because of the deep penetration of microwave energy and the low thermal loss by conduction. Satisfactory cellulose pellet densities for these studies are $1.56 \text{ g}/\text{cm}^3$ at 21°C .

In Figure 2, the dashed line presents the absorbed microwave power as a function of time. The absorbed power was determined by recording continuously the difference in the detectors positioned before and after the reaction zone. Attenuation within the reaction zone was accounted for by noting the power absorbed without any cellulose in the reactor.

As mentioned before, dry cellulose does not transform electromagnetic energy efficiently, and because of this there is a low level of absorption in the initial 30–45 sec of each experiment. Some heating, nevertheless, does occur, and as the temperature rises there is a rapid increase in absorption. An increasing temperature adversely affects the degree of crystallinity in the cellulose fibers, opening new areas for high-frequency interaction. As the loss factor increases and the temperature builds, a significant amount of chemical dehydration (not evaporation) occurs, and before this moisture has a chance to diffuse to the surface of the cellulose pellet there is a rapid increase in both the absorption of energy and the temperature. The loss factor of water is approximately 60 times greater than that of cellulose at 2450 MHz.³⁸ As a result, it is these water mol-

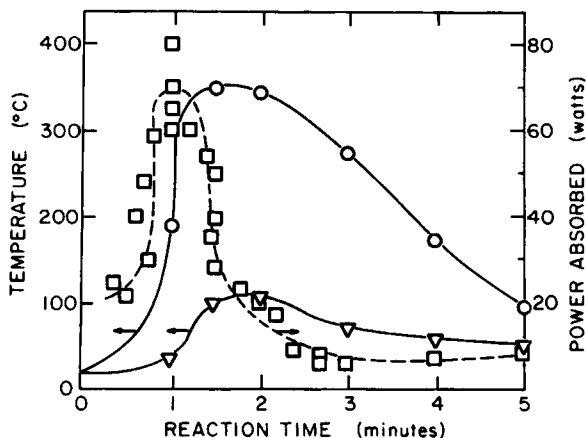


Fig. 2. Internal pellet temperature (O), external gas temperature (∇), and absorbed power (□) vs. microwave exposure time for 2.6 g of cellulose.

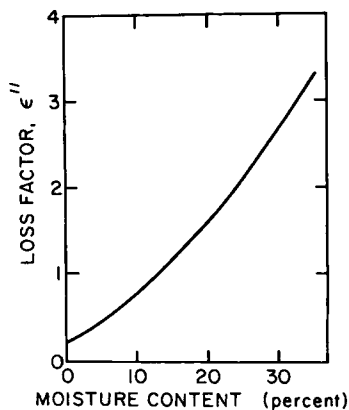


Fig. 3. Dielectric loss factor for paper (cellulose) as a function of moisture content for microwave irradiation at 2450 MHz and 22°C (ref. 39).

ecules which actually absorb a large part of the energy spike that is observed in Figure 2 during the first minute of microwave exposure. An indication of the magnitude of this effect is shown in Figure 3 from Metaxas and Driscoll,³⁹ where the relationship between the loss factor and the moisture content for paper at 2450 MHz and 22°C is given. Because the absorption of power is directly proportional to the loss factor, increasing the moisture content of dry cellulose to 10% produces a 400% increase in the amount of power absorbed. As can be seen in Figures 4 and 5, it was during the period of high-energy absorption that the reaction proceeded at its highest rate. With 2.5–2.7 g of cellulose in the reactor, a period of only 0.85 min was required before the amount of absorbed energy began to fall. This period corresponds to the linear portion of Figure 5.

This rapid decrease in the loss factor was due to a decrease in the moisture content, the polarity of the polysaccharide, and the amount of material in the reactor. Infrared spectra of cellulose and charred residue are shown in Figure 6 (curves b and c), and when the two spectra are compared it is obvious that the degree of degradation was extensive. There is a significant decrease in the ab-

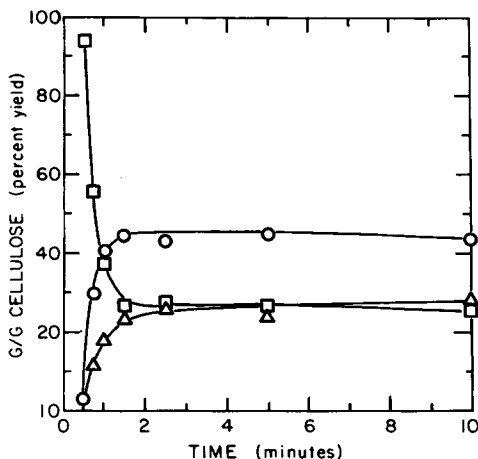


Fig. 4. Yield of pyrolysis products as a function of microwave exposure time for 2.6 g of cellulose. (O) tar, (Δ) condensate, and (□) charred residue.

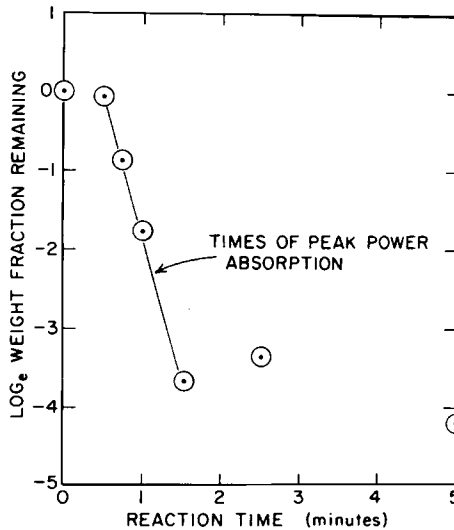


Fig. 5. Devolatilization kinetics. $\text{Log}_e (w - w^*) / (w_0 - w^*)$ vs. time for data of Fig. 2. Least-squares fit to only those which correspond to peak power absorption.

sorption bands around 3.0 and 9.5 μm because of a reduction in the number of polar hydroxide groups. In addition, the infrared spectra show an increase in the absorption maxima around 5.85 and 6.25 μm . Absorption in these regions are due to carbonyl and unsaturated ethylenic linkages ($>\text{C}=\text{C}<$).

Because nonoxidative helium atmospheres were used in most experiments, oxidation cannot be an acceptable explanation for the occurrence of carbonyl

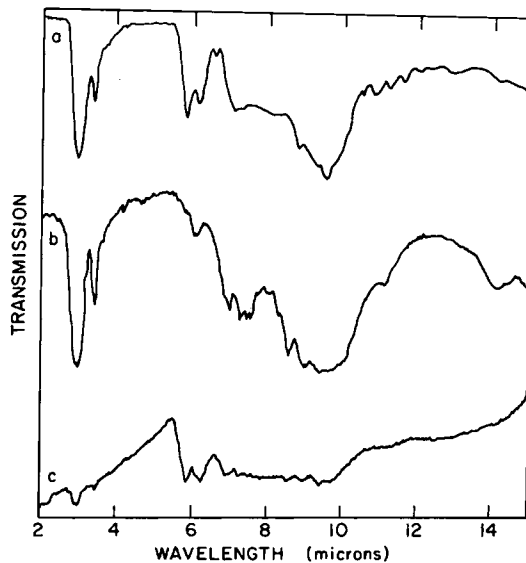


Fig. 6. Infrared absorption spectra of cellulose filter paper and pyrolysis products after 5 min exposure time. (a), Tar (b), cellulose and (c) charred residue.

groups. Unsaturation and carbonyl formation can best be explained by the extensive cleavage and dehydration reactions that are known to occur under pyrolytic conditions.^{9-13,40-45} Carbonyl groups are formed when the oxygen bonds of the pyranose rings are fractured. This is usually followed by rearrangement to furanoid rings or random cleavage of the oxygen bonds liberating volatile products.⁴⁰

As shown in Figure 2, a peak internal pellet temperature, measured by the intermittent procedure described earlier, was 350°C. This temperature was reached within 1.5 min when 2.6 g of pure dry cellulose was exposed to a power density of 130 W/cm² of waveguide. To obtain an estimate of the gas temperature and heat loss in our experiment, a thermocouple was placed immediately after the reaction zone and the temperature of the passing gas was recorded. The gas temperature, indicated by triangles, is also given in Figure 2. The maximum gas temperature achieved, with a helium purge rate of 0.249 g/hr, was 108°C. This is considerably lower than the temperatures obtained within the interior of the cellulose pellets and accounts for a loss of approximately 0.018 W when averaged over a 5-min reaction period at atmospheric pressures. The energy loss was calculated from

$$\text{energy loss} = (\int C_P dT) F_m t$$

where C_P is the heat capacity of helium, T is the temperature, F_m is the average mass flow rate, and t is the time of flow. As shown by Work,³⁶ this loss is less than 0.1% of the overall energy needed to carry out the pyrolysis reactions. From the standpoint of energy conservation, this rapid response and reverse temperature gradient can significantly reduce the amount of heat that is inefficiently lost to the surrounding environment.

The lower external gas temperature compared to the higher pellet core temperature is labeled a reverse temperature gradient and would be expected in conventional furnaces in the case of exothermic reactions. Other reverse temperature gradients have been observed in microwave food processing, and it appears that the uniform heating from the interior is responsible for the rapidity of processing times. It has been suggested by several authors^{3,46,47} that the rate of reaction in a low conductivity, large diameter solid such as biomass or coal pellets is often limited by the heat transfer rate. It appears that in microwave absorption or heating the reaction rate is determined by the temperature dependent property, the dielectric loss constant of the medium. By introducing inert additives to the substrate, the dielectric loss properties can be altered. Current studies are in progress to control and increase the absorption of microwave energy.⁴⁷

Microwave volume heating forces volatiles out of the porous substrate more quickly because of increased internal pressure as the cellulose is volatilized. The entire solid volatilizes at once as opposed to a reacting interface moving inward. Once the volatiles leave the solid reactant and char they will be exposed to a relatively lower gas temperature (see Figs. 2 and 4) than would exist in a conventional furnace with external heating of the pellet through its surface. Fewer secondary reactions and a compressed reaction time even for a large pellet occur, as expected.

Reaction Time

As in other pyrolytic studies of cellulose, the degradation products were divided into four major fractions: charred residue, viscous tars, condensable volatiles, and fixed gases. The formation rate of these product fractions is shown in Figure 4. If one uses the weight loss data to yield an apparent rate constant for devolatilization which can be compared to other studies,^{7,10} the initial data suggest a pseudo-first-order rate equation of the following form for the first minute of the experiment after an initial induction period (see Fig. 5):

$$\ln(w - w^*)/(w_0 - w^*) = -kt$$

where w_0 is the initial weight of cellulose, w^* is the weight at $t = \infty$, and t is the time of reaction in min. The apparent rate constant from Figure 5 is about 3.5 min^{-1} , which is high especially in view of the large pellet size.

It is often difficult to compare cellulose pyrolysis rate coefficients derived from several studies. Many articles do not provide sufficient detail to allow the reader to evaluate whether the sample temperature was uniform and at the oven temperature (no heat transfer limitation) or whether the volatiles rapidly left the reaction zone and escaped further degradation (no mass transfer limitation). All of the studies reviewed in the article by Lewellyn et al.⁷ reported rate coefficients slower than Lewellyn's, save one.⁴⁸ The latter's rate coefficient is higher, but only over a portion of the temperature range studied. Thus, one might conclude that data inconsistency might arise from slow heat transfer retarding the rate. Shafizadeh et al.¹¹ address this problem by reporting an "apparent heat transfer rate coefficient" of 2.92 min^{-1} . This value is an indication of the time required for sample and oven temperature to achieve the same value and is used to correct the temperatures. It is noteworthy in the study by Shafizadeh et al. that the apparent heat-up rate is nearly the same as the devolatilization rate.

Although the lack of an isothermal experiment, inaccurate temperature results, and the nature of the microwave absorption precluded exact kinetics measurements in this preliminary study, it can be concluded in view of our large pellet size that our devolatilization is indeed rapid. Table I is a compilation of recent rate coefficients for cellulose devolatilization that were not reviewed by Lewellyn.⁷ In order to make a useful comparison to this work, a column in Table I indicates the temperature at which the reported rate coefficients are about equal to 3.5 min^{-1} , the apparent rate coefficient of this study. A two-step pyrolysis mechanism for cellulose is indicated by Bradbury et al.¹⁰ and Roberts,⁴⁹ and both expressions are included. Fairbridge⁵⁰ used oxidizing atmospheres. Since the calculated temperatures are within 25–50°C of our measured approximate value of 350°C internal pellet temperature, it is concluded that the intrinsic kinetics in a large pellet are being measured. This is substantiated by the primary products discussed below. Moreover, in spite of a low-confidence temperature measurement (350°C is our approximate peak temperature, achieved after less than 1 min), only the study by Bradbury et al.¹⁰ appears to show a faster rate than that observed here and after a substantially longer heat-up time. Thus microwave heating compresses the reaction time. Current efforts are in progress to model the nonisothermal kinetics and understand heat transfer in the large pellets.

TABLE I
Cellulose Devolatilization Rate Expressions and Calculated Temperatures at which Rates are Comparable to those Found in Microwave Heating

Investigator	Reported rate coefficient (min ⁻¹) E_a in kcal mole	Temperature range of study (°C)	By extrapolating rate expression, Temperature at which rate coefficient equals 3.5 min ⁻¹ (°C)
Lewellyn et al. (1976) (ref. 7)	$4.07 \times 10^{11} \exp(-33.4/RT)$	250–1100	$T \approx 382$
Bradbury et al. (1979) (ref. 10)	$7.9 \times 10^{11} \exp(-36.6/RT)$	259–341	$T \approx 427$
Fairbridge et al. (1978) (ref. 50)	$1.7 \times 10^{21} \exp(-58/RT)$	259–341	$T \approx 335$
	$1.8 \times 10^{12} \exp(-32.2/RT)$	275–340	$T \approx 324$
(used oxidizing atmosphere)	$2.6 \times 10^{20} \exp(-59.3/RT)$	275–340	$T \approx 375$

Product Distribution

As shown in Table II, the major products are carbon dioxide, water, furfural, levoglucosan, and charred residue. These are the same compounds that others have found by studying the thermal pyrolysis of cellulose, using conditions that have varied extensively. A few representative results from the work of others are included in Table II for comparison purposes.

The yields of both furfural and levoglucosan in this study indicate that a great deal of activity was centered around the bonds between the first carbon atom and the backbone oxygen in the cellulose chain which are necessarily cleaved for the formation of both chemicals. Owing to the strong electron withdrawing effect of oxygen atoms, much of the dipole interaction that occurs between microwaves and cellulose is due to hydrogen–oxygen and carbon–oxygen bonds. It seems reasonable that these bonds would receive a greater portion of the energy that is dissipated in the macromolecule, increasing the probability of cleavage and enhancing the formation of furfural and levoglucosan. The furfural yield is reproducible and is somewhat higher than that noted in other studies.⁵¹

The furfural and water were part of the fraction collectively called “condensable volatiles.” The amount of water by weight in this aqueous fraction varied from 92 to 95%. When based on the initial weight of cellulose, the average overall water yield was 23% (power density 130 W/cm², microwave exposure time 5 min). This represents on the average about 2.1 water molecules per glucose monomer in the polysaccharide. Undoubtedly, a small amount of this water was included within the cellulose fibers and physically absorbed on the fiber surface, but because of the drying procedure used, this amount was minor. The magnitude of this effect was determined by a solvent replacement procedure outlined by Staudinger et al.⁵³ When prepared by this method, cellulose was exposed to microwave irradiation under identical conditions and there was no detectable difference in the pyrolysis pattern relative to that in which cellulose was dried in the vacuum desiccator. The overall yield of the various fractions were the same within experimental error, and there was no significant change in the amount of water recovered.

In addition to water, the remaining 5–8% of the aqueous condensate fraction

TABLE III
Relative Mass Concentration of the Organic Volatiles from Microwave Pyrolysis of Cellulose

Peak No.	Compound	Relative mass concentration ^a		Relative retention time (Furfural = 1.0)	Identification ^b
		A (%)	B (%)		
1	Acetaldehyde	5.6	5.4	0.012	P
2	Furan	—	0.3	0.042	P
3	Acetone	2.1	0.6	0.060	P
4	Propanal	3.5	5.3	0.077	P
5	Methanol	—	trace	0.131	P
6	n-Butanal	3.9	2.1	0.143	P
7	2,3 Butadione	2.7	7.9	0.196	P
8		—	1.4	0.232	
9	Crotonaldehyde	2.7	2.9	0.286	T
10		—	1.6	0.524	
11			—	—	
12		2.1	1.8	0.560	
13		—	4.1	0.690	
14		2.0	4.4	0.839	
15		—	1.7	0.857	
16		2.4	0.1	0.923	
17		—	0.1	0.964	
18		0.5	1.5	0.976	
19	Furfural	57.0	24.0	1.000	P
20		0.7	0.2	1.040	
21	2 Furyl methyl ketone	5.2	2.6	1.090	T
22		—	2.3	1.110	
23		—	1.9	1.120	
24		—	0.2	1.170	
25		—	trace	1.210	
26	5 Methyl furfural	7.6	4.6	1.230	T
27		0.6	0.1	1.270	
28		—	10.7	1.440	
29		1.0	0.2	1.510	
30		0.3	trace	1.540	
31		—	2.3	1.810	

^a Percentage in these columns are based on the integrated response of the gas chromatogram. (A) Pyrolysis of 2.6 g of pure cellulose with 130 W/cm² in helium at 550 torr. (B) Pyrolysis of 2.6 g of cellulose treated with 0.47% NaOH (by weight) with 130 W/cm² helium atmosphere at 550 torr.

^b P, positive identification; T, tentatively identified.

included a wide variety of low-molecular-weight compounds, most of which were aldehydes. A representative chromatogram from this fraction is shown in Figure 7 and a list of the identified compounds is given in Table III. Comparison of these products to that of Schwenker⁵⁴ shows numerous similarities in the identified products despite the use of microwave heating in this study and similar conditions but conventional heating in Schwenker's work.

After several gas chromatographic analyses using many different conditions, it was concluded that only carbon dioxide and carbon monoxide were present in detectable amounts in the gaseous fraction of the pyrolysis products. The yield of carbon dioxide varied from 3 to 5% when based on the initial weight of cellulose. With the experimental apparatus used, the yield of carbon monoxide

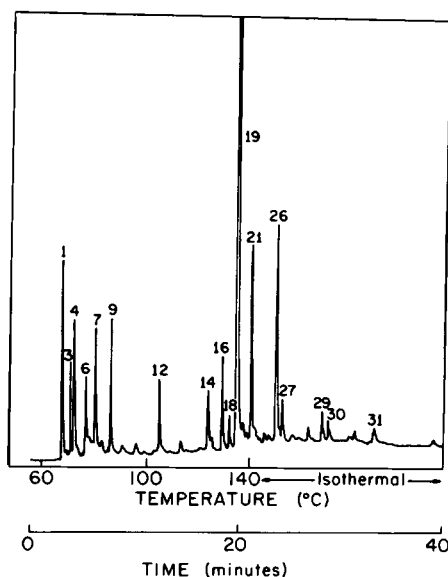


Fig. 7. Gas chromatogram of volatile products from microwave pyrolysis of cellulose in helium.

could not be determined accurately because of the reduced pressures. However, as determined by a mass balance, the amount was always less than 2%.

Potentially, the most useful fraction was the tars. At slightly elevated temperatures (400–500°C) this material has the consistency of a viscous fluid. In order to determine the chemical composition of this fraction, a gas chromatogram was taken by preparing trimethylsilyl derivatives. Only four compounds were revealed (Table IV), and a representative copy of one of the chromatograms is shown in Figure 8. As can be seen, levoglucosan with a retention time somewhat less than that of α glucose was present in very high concentrations. Peak No. 4 was not identified, but by comparing these results to those obtained by Shafizadeh, it is likely that 1,6-anhydro- β -D-glucofuranose was responsible for this peak. From the integrated chromatographic response, it was determined that levoglucosan accounted for approximately 90% of the tar fraction, and when based on the initial weight of cellulose, an overall yield of 39% was obtained.

An infrared spectra of the tar fraction was given in Figure 6 (curve a) shows

TABLE IV
Relative Mass Concentration of the Trimethylsilyl Tar Derivatives from Microwave Pyrolysis of Cellulose^a

Peak No.	Compound	Relative mass concentrations ^b	Identification ^c
1	Petroleum ether	solvents	P
2	Pyridine	solvents	P
3	Levoglucosan	90.5%	P
4	1,6-anhydro β -D-glucofuranose	trace	T
5	α -glucose	4.7%	P
6	β -glucose	4.8%	P

^a Pyrolysis of 2.6 g of pure cellulose with 130 W/cm² in helium at 550 torr.

^b Percentage in these columns are based on the integrated response of the gas chromatogram.

^c P, positive identification; T, tentatively identified.

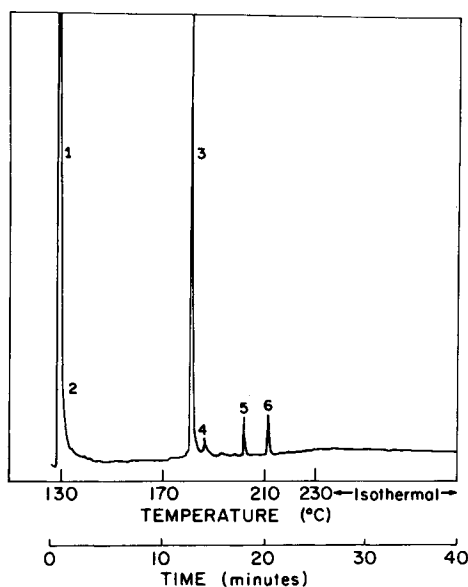


Fig. 8. Gas chromatogram of trimethylsilyl tar derivatives of condensate fraction from microwave pyrolysis of cellulose in helium.

a very close resemblance to that of pure levoglucosan (Fig. 9).⁴⁰ In addition to this anhydrosugar, the infrared spectra of the tar indicated that carbonyl and unsaturated ethylenic linkages were also present (absorption maxima at 5.85 and 6.25 μm). Although compounds of this nature were not indicated in the gas chromatographic analysis, the occurrence of these absorption bands was not surprising. Several studies have found small amounts of 5-hydroxymethyl-2-furaldehyde, 2-furyl hydroxymethyl ketone, and other compounds partially condensed within the tar fraction.^{40,42-45,51}

Effect of Power on Product Distribution

Because pure cellulose has a very low loss factor, the strength of the electric field in eq. (1) plays an important part in determining the level of activity that exists between cellulose and microwaves. As the field strength increases, the power absorbed increases as the square of the field strength. Preliminary data on this effect is shown in Figure 10, where the yield of the various pyrolysis products is given as a function of the power input.

The power intensity (130 W/cm²) reported in the other figures corresponds in Figure 10 to the 2000-W input power divided by the cross-sectional area of

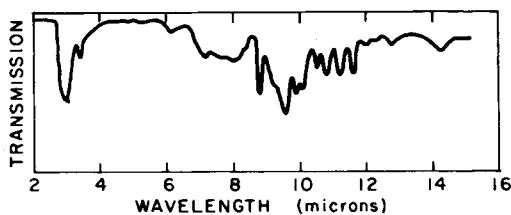


Fig. 9. Infrared absorption spectrum of levoglucosan (ref. 40).

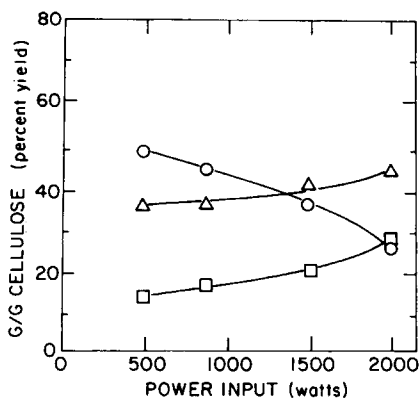


Fig. 10. Yield of pyrolysis products as a function of power for a 5-min exposure. (Δ) Tar, (\square) condensables, and (\circ) charred residue.

the waveguide. Increased char yield at lower power input is consistent with a lower extent of reaction during the period of peak absorption. However, since detailed product analyses and spectra were not obtained for these experiments, this is only speculation.

As the power was increased, there was a substantial decrease in the amount of charred residue, indicating that sufficient energy was available to produce the random bond cleavages that are necessary for the formation of carbon dioxide, water, and other volatile products. It is interesting to speculate that the tar yield appears to be less sensitive to the power intensity than either of the other two products shown. This indicates that perhaps the transglycosylation reactions require only a low threshold of microwave energy, and thus this form of energy is effective even at low power intensities.

Effect of Pressure on Product Distribution

It has been demonstrated by Russel et al.³ that the rate of mass transfer from the porous particle interior to the pellet exterior is one of the slower processes to occur in pyrolysis systems. Of the mass transport occurring inside the pellet, diffusion and pressure-driven outflow, volatiles outflow is more rapid.^{35,47,49} The use of very thin samples and, at times reduced pressures enabled Lewellyn et al.⁷ to volatilize cellulose completely with no char yield. Shafizadeh⁴⁰ and Bradbury et al.,¹⁰ however, required pressures on the order of a few hundred Pa to achieve a tar yield of approximately 30–40%. When atmospheric pressures were used, tar yields were reduced by as much as 65%, presumably because of the decreased escape rate of the volatiles from the hot reaction zone where secondary reactions occur. In this study, no effect on gross product fractions was observed from 3.33×10^4 Pa (250 torr) to 1 atm as shown in Figure 11, and levoglucosan yields were typical of the low pressure data of Shafizadeh.⁴⁰ No effect of pressure over the range studied is observed, owing to the already rapid volatiles outflow caused by internal pressure gradients. However, judging from the model results of Russel et al.,³ the point at which hydrogen pressure effects on devolatilization rates and char yield become noticeable is at least an order of magnitude higher in pressure. Although a wider pressure range needs to be evaluated, the experimental apparatus cannot operate above atmospheric pressure and a plasma forms in the reaction zone below the minimum pressure in Figure 11.

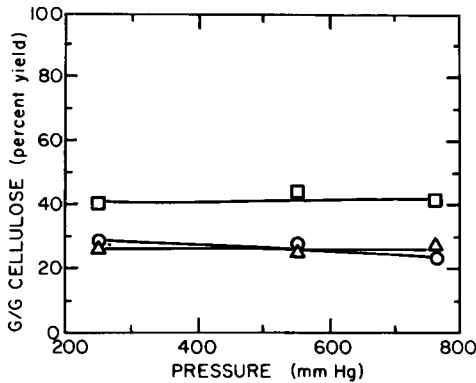


Fig. 11. Yield of pyrolysis products as a function of pressure for a 5-min exposure. (\square) Tar, (Δ) condensables, and (\circ) charred residue.

SUMMARY AND CONCLUSIONS

The results of this study indicate that even at low absorption, dielectric loss microwave pyrolysis of cellulose is a more rapid process and gives increased tar yield at somewhat elevated pressures from 3.33×10^4 to 1.03×10^5 Pa (250 torr–1 atm) relative to conventional pyrolysis studies. An explanation consistent with these observations and the results of others is that in dielectric loss microwave heating, heat transport limitations are overcome by volume heating of the particle. Heating rate and therefore devolatilization rate are determined by the temperature-dependent property of the material, the dielectric loss factor. Owing to volume heating and low external gas temperature, primary volatiles, upon stabilization, appear to yield levoglucosan and carbon oxides. A model to predict volume heating pyrolysis rate is under development. Since the additional cost of particle size reduction would add to the already tenuous economics of biomass chemical conversion, rapid microwave pyrolysis of large particles might offer an advantage. Current efforts focus on the alterations in product slates that can be produced by changing heat transfer rates in the solid and maintaining low gas temperatures in the gas phase.

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